

## 8.9: Distillation

### Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Sketch out a typical *boiling point diagram* for a binary liquid solution, and use this to show how a simple one-stage *distillation* works.
- Explain the role of the *lever rule* in fractional distillation
- Describe the purpose and function of a *fractionating column*
- Sketch out boiling point diagrams for high- and low-boiling *azeotropes*
- Describe the role of distillation in *crude oil refining*, and explain, in a very general way, how further processing is used to increase the yield of gasoline motor fuel.

Distillation is a process whereby a mixture of liquids having different vapor pressures is separated into its components. At first one might think that this would be quite simple: if you have a solution consisting of liquid A that boils at 50°C and liquid B with a boiling point of 90°C, all that would be necessary would be to heat the mixture to some temperature between these two values; this would boil off all the A (whose vapor could then be condensed back into pure liquid A), leaving pure liquid B in the pot. But that overlooks that fact that these liquids will have substantial vapor pressures at *all* temperatures, not only at their boiling points.

### Vapor Pressure vs. Composition Phase Diagrams

To fully understand distillation, we will consider an ideal binary liquid mixture of A and B. If the **mole fraction** of A in the mixture is  $\chi_A$ , then by the definition of mole fraction, that of B is

$$\chi_B = 1 - \chi_A \quad (8.9.1)$$

Since distillation depends on the different vapor pressures of the components to be separated, let's first consider the vapor pressure vs. composition plots (Figure 8.9.1) for a hypothetical mixture at some arbitrary temperature at which both liquid and gas phases can exist, depending on the total pressure.

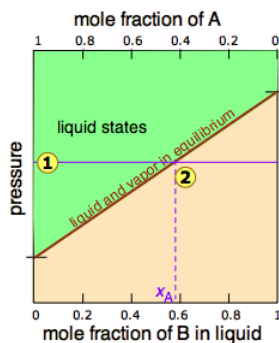


Figure 8.9.1: Liquid-Vapor Equilibrium curve.

In Figure 8.9.2, all states of the system (i.e., combinations of pressure and composition) in which the solution exists solely as a **liquid** are shaded in green. Since liquids are more stable at higher pressures, these states occupy the upper part of the diagram. At any given total vapor pressure such as at ①, the composition of the vapor in equilibrium with the liquid (designated by  $x_A$ ) corresponds to the intercept with the diagonal equilibrium line at ②. The diagonal line is just an expression of the linearity between vapor pressure and composition according to **Raoult's law**.

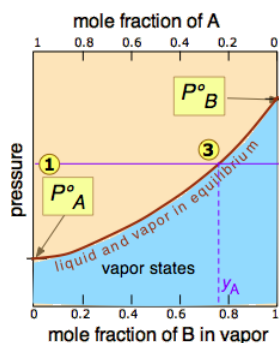


Figure 8.9.2: Liquid-Vapor Equilibrium curve.

③  
 of the pressure line  
 ①  
 with the equilibrium curve defines the mole fractions of  
 A  
 and  
 B  
 present in the vapor. (Note that mole fractions of gases, which we are dealing with here, are conventionally represented by  
 $y$   
 , hence  
 $y_A$   
 and  
 $y_B$   
 ). The curvature of the equilibrium line arises from the need to combine  
 Raoult's law  
 with  
 Dalton's law of partial pressures  
 which applies to gaseous mixtures.

Figure 8.9.3.

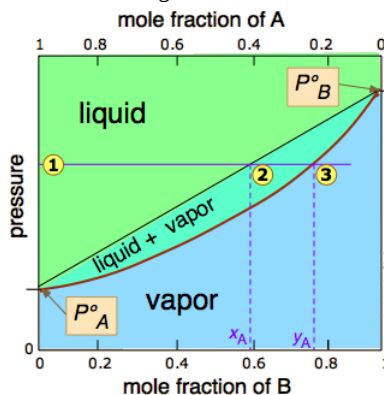


Figure 8.9.3

The two liquid-vapor equilibrium lines (one curved, the other straight) now enclose an area in which liquid and vapor can **coexist**; outside of this region, the mixture will consist entirely of liquid or of vapor. At this particular pressure ①, the intercept ② with the upper boundary of the two-phase region gives the mole fractions of A and B in the liquid phase, while the intercept ③ with the lower boundary gives the mole fractions of the two components in the vapor.

### ? Exercise 8.9.1

Take a moment to study Figure 8.9.5 and to confirm that

- because both intercepts occur on equilibrium lines, they describe the *compositions* of the liquid and vapor that can simultaneously exist;
- the compositions of the vapor and liquid are not the same;
- in the vapor, the mole fraction of B (the more volatile component of the solution) is greater than that in the liquid;

- in the liquid, the mole fraction of A (the less volatile component) is smaller than that of the vapor.

The vapor in equilibrium with a solution of two or more liquids is **always** richer in the more volatile component.

## Temperatures vs. Composition Phase Diagrams (Boiling Point Diagrams)

The rule shown above suggests that if we heat a mixture sufficiently to bring its total vapor pressure into the two-phase region, we will have a means of separating the mixture into two portions which will be enriched in the more volatile and less volatile components respectively. This is the principle on which distillation is based. But what temperature is required to achieve this? Again, we will spare you the mathematical details, but it is possible to construct a plot similar to the Figure 8.9.4 except that the vertical axis represents *temperature* rather than pressure. This kind of plot is called a *boiling point diagram*.

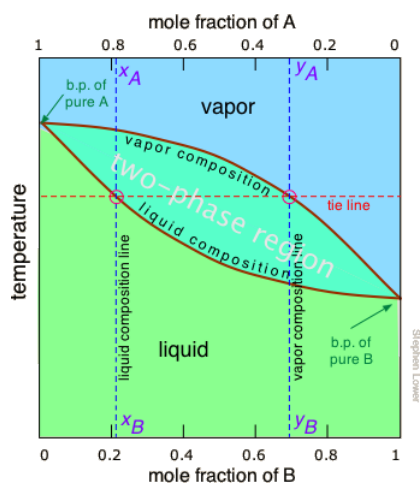
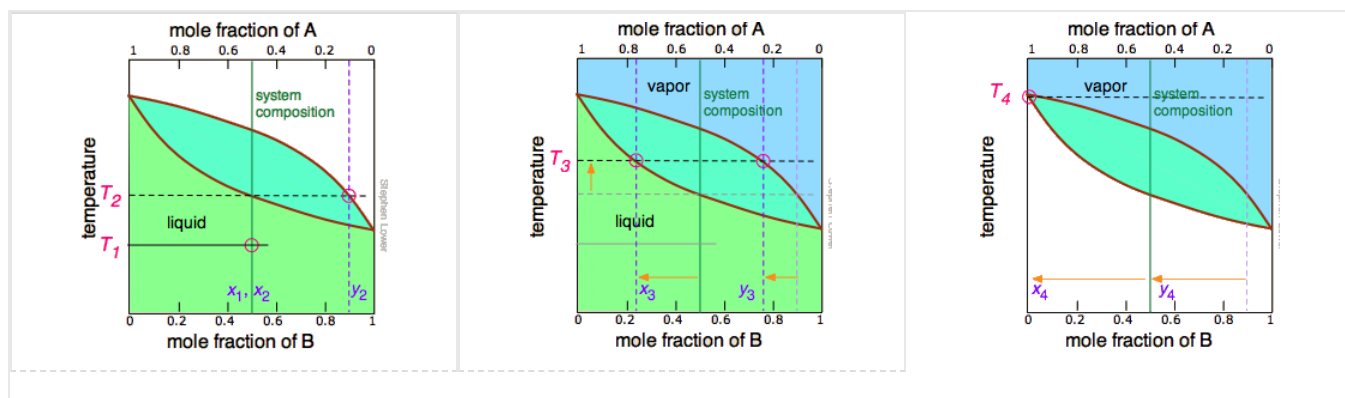


Figure 8.9.4: Boiling point diagram of a volatile two-component system.

Some important things to understand about Figure 8.9.6:

- The shape of the two-phase region is bi-convex, as opposed to the half-convex shape of the pressure-composition plot.
- The slope of the two-phase region is opposite to what we saw in the previous plot, and the areas corresponding to the single-phase regions are reversed. This simply reflects the fact that liquids having a higher vapor pressure boil at lower temperatures, and *vice versa*.
- The horizontal line that defines the temperature is called the *tie line*. Its intercepts with the two equilibrium curves specify the composition of the liquid and vapor in equilibrium with the mixture at the given temperature.
- The vapor composition line is also known as the *dew point line* — the temperature at which condensation begins on cooling.
- The liquid composition line is also called the *bubble point line* — the temperature at which boiling begins on heating.

The tie line shown in Figure 8.9.6 is for one particular temperature. But when we heat a liquid to its boiling point, the composition will change as the more volatile component (B in these examples) is selectively removed as vapor. The remaining liquid will be enriched in the less volatile component, and its boiling point will consequently rise. To understand this process more thoroughly, let us consider the situation at several points during the distillation of an equimolar solution of A and B.



**Figure 8.9.5A:** We begin with the liquid at  $T_1$ , below its boiling point. When the temperature rises to  $T_2$ , boiling begins and the first vapor (and thus the first drop of condensate) will have the composition  $y_2$ .

**Figure 8.9.5B:** As the more volatile component B is boiled off, the liquid and vapor/condensate compositions shift to the left (orange arrows).

**Figure 8.9.5C:** At  $T_4$ , the last trace of liquid disappears. The system is now entirely vapor, of composition  $y_4$ .

Notice that the vertical green *system composition* line remains in the same location in the three plots because the "system" is defined as consisting of both the liquid in the "pot" and that in the receiving container which was condensed from the vapor. The principal ideas you should take away from this are that

- distillation can never completely separate two volatile liquids;
- the composition of the vapor and thus of the condensed distillate changes continually as each drop forms, starting at  $y_2$  and ending at  $y_4$  in this example;
- if the liquid is completely boiled away, the composition of the distillate will be the same as that of the original solution.

## Laboratory Distillation Setup

The apparatus used for a simple laboratory batch distillation is shown here. The purpose of the thermometer is to follow the progress of the distillation; as a rough rule of thumb, the distillation should be stopped when the temperature rises to about half-way between the boiling points of the two pure liquids, which should be at least 20-30 °C apart (if they are closer, then *fractional distillation*, described below, becomes necessary).

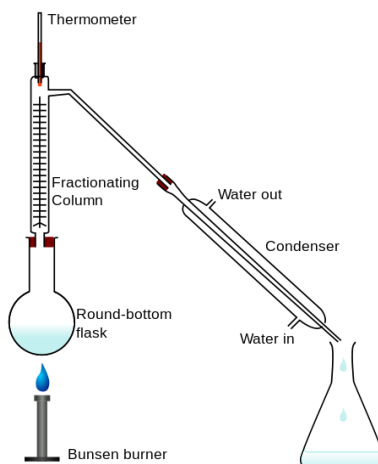


Figure 8.9.6: Fractional distillation setup. An Erlenmeyer flask is used as a receiving flask. Here the distillation head and fractionating column are combined in one piece. from Wikipedia

Condensers are available in a number of types. The simple *Liebig condenser* shown above is the cheapest and therefore most commonly used in student laboratories. Several other classic designs increase the surface area separating the vapor/distillate and cooling water, leading to greater heat exchange efficiency and allowing higher throughput.

## Fractional Distillation

Although distillation can never achieve complete separation of volatile liquids, it can in principal be carried out in such a way that any desired degree of separation can be achieved if the solution behaves ideally and one is willing to go to the trouble. The general procedure is to distill only a fraction of the liquid, the smaller the better. The condensate, now enriched in the more volatile component, is then collected and re-distilled (again, only a small fraction), thus obtaining a condensate even-more-enriched in the more volatile component. If we repeat this sequence many times, we can eventually obtain almost-pure, if minute, samples of the two components.

But since this would hardly be practical, there is a better way. In order to understand it, you need to know about the *lever rule*, which provides a simple way of determining the relative *quantities* (not just the compositions) of two phases in equilibrium. The lever rule is easily derived from **Raoult's** and **Dalton's laws**, but we will simply illustrate it graphically (Figure 8.9.7). The plot shows the boiling point diagram of a simple binary mixture of composition ①. At the temperature corresponding to the tie line, the composition of the liquid corresponds to ② and that of the vapor to ③.

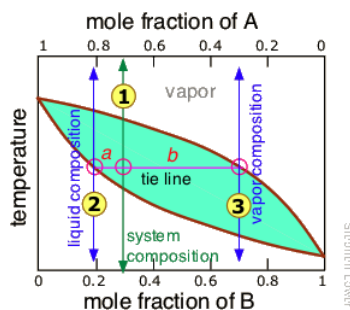


Figure 8.9.7:

So now for the lever rule: the relative quantities of the liquid and the vapor we identified above are given by the lengths of the tie-line segments labeled  $a$  and  $b$ . Thus in this particular example, in which  $b$  is about four times longer than  $a$ , we can say that the mole ratio of vapor (of composition ③) to liquid (composition ②) is 4.

### Steps in Fractional Distillation

It is not practical to carry out an almost-infinite number of distillation steps to obtain nearly-infinitesimal quantities of the two pure liquids we wish to separate. So instead of collecting each drop of condensate and re-distilling it, we will distill half of the mixture in each step. Suppose you want to separate a liquid mixture composed of 20 mole-% B and 80 mole-% A, with A being the more volatile.

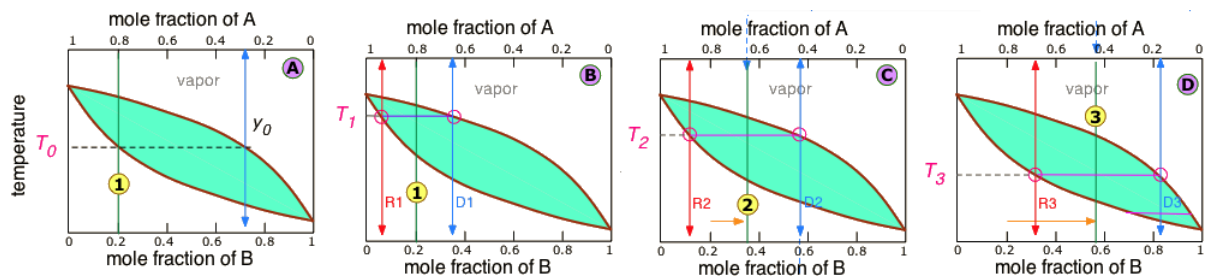


Figure 8.9.8: Steps in Fractional Distillation

**A** As we heat the mixture whose overall composition is indicated by ①, the first vapor is formed at  $T_0$  and has the composition  $y_0$ , found by extending the horizontal dashed line until it meets the vapor curve. This vapor is clearly enriched in B; if it is condensed, the resulting liquid will have a mole fraction  $x_B$  approaching that of A in the original liquid. But this is only the first drop, we don't want to stop there!

**B** As the liquid continues to boil, the boiling temperature rises. When it reaches  $T_1$ , we will have boiled away half of the liquid. At this point, the "system" composition (liquid plus vapor) is still the same (①), but is now equally divided between the liquid, which we call "residue"  $R_1$ , and the condensed vapor, the *distillate*  $D_1$ .

*How do we know it is equally divided? We have picked  $T_1$  so that the tie line is centered on the system concentration, so by the lever rule,  $R_1$  and  $D_1$  contain equal numbers of moles.*

**C** We now take the condensed liquid  $D_1$  having the composition ②, and distill half of it, obtaining distillate of composition  $D_2$ .

**D** .. and then carry out yet another distillation, this time using  $D_3$  as our feedstock.

**E** Our four-stage fractionation has enriched the more volatile solute from 20 to slightly over 80 mole-percent in  $D_4$ . The less volatile component A is most concentrated in  $R_1$ .  $R_2$  through  $R_4$  are thrown away (but not down the sink, please!)

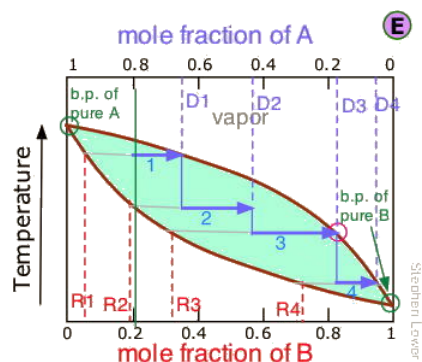


Figure 8.9.9: Boiling point diagrams illustrating fractional distillation"

This may be sufficient for some purposes, but we might wish to do much better, using perhaps 1000 stages instead of just 4. What could be more tedious?

### Fractionation with reflux

Not to worry! The multiple successive distillations can be carried out "virtually" by inserting a *fractionating column* between the boiling flask and the condenser.

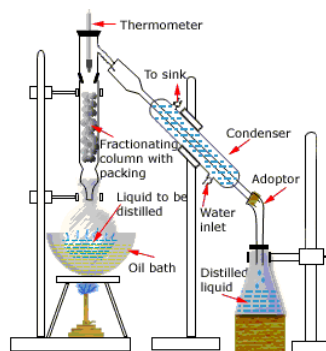


Figure 8.9.10:

These columns are made with indentations or are filled with materials that provide a large surface area extending through the vertical temperature gradient (higher temperature near the bottom, lower temperature at the top.) The idea is that hot vapors condense at various levels in the column and the resulting liquid drips down (*refluxes*) to a lower level where it is vaporized, which corresponds roughly to a re-distillation.



*Vigreux columns* having multiple indentations are widely used (above right). Simple columns can be made by filling a glass tube with beads, short glass tubes, or even stainless steel kitchen-type scouring pads. More elaborate ones have spinning steel ribbons.

### Separation efficiency: theoretical plates

The operation of fractionating columns can best be understood by reference to a bubble-cap column. The one shown here consists of four sections, or "plates" through which hot vapors rise and bubble up through pools of condensate that collect on each plate. The intimate contact between vapor and liquid promotes equilibration and re-distillation at successively higher temperatures at each higher plate in the column. Unlike the case of the step-wise fractional distillation we discussed above, none of the intermediate residues is thrown away; they simply drip down back into the pot where their fractionation journey begins again, always leading to a further concentration of the less-volatile component in the remaining liquid. At the same time, the vapor emerging from the top plate (5) provides a continuing flow of volatile-enriched condensate, although in diminishing quantities as it is depleted in the boiling pot.

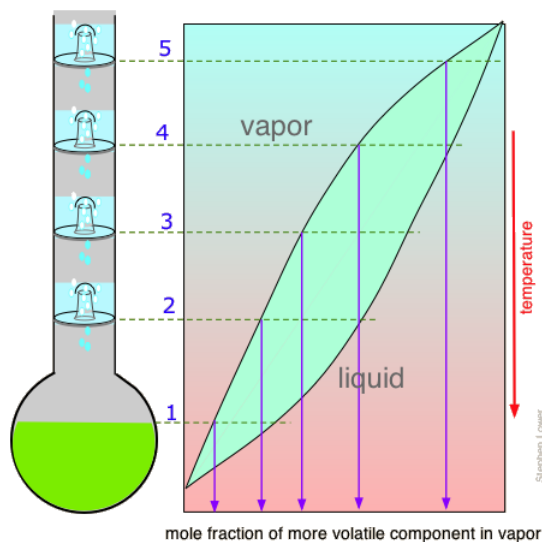


Figure 8.9.11:

If complete equilibrium is attained between the liquid and vapor at each stage, then we can describe the system illustrated above as providing "five theoretical plates" of separation (remember that the pot represents the first theoretical plate.) Equilibrium at each stage requires a steady-state condition in which the quantity of vapor moving upward at each stage is equal to the quantity of liquid draining downward — in other words, the column should be operating in total reflux, with no net removal of distillate. So any real distillation process will be operated at a reflux ratio that provides optimum separation in a reasonable period of time.

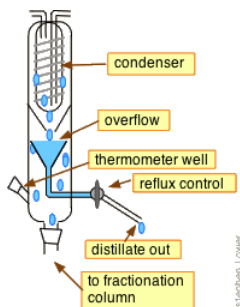


Figure 8.9.11: Reflux ratio can be adjusted by placing a special control head on top of the fractionation column. The laboratory-type device shown here illustrates the general concept. Reflux control is mainly of importance in large-scale industrial operations.

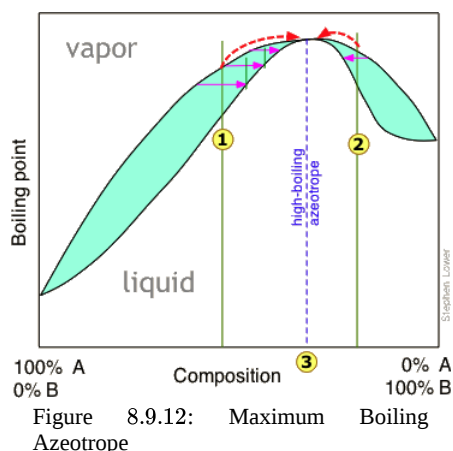
Some of the more advanced laboratory-type devices (such as some spinning-steel band columns) are said to offer up to around 200 theoretical plates of separating power.

## Azeotropes: the Limits of Distillation

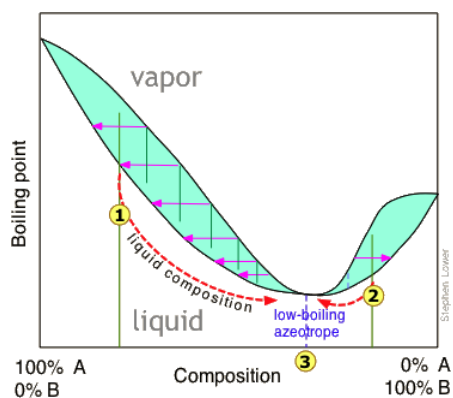
The boiling point diagrams presented in the foregoing section apply to solutions that behave in a reasonably ideal manner — that is, to solutions that do not deviate too far from Raoult's law. As we explained above, mixtures of liquids whose intermolecular interactions are widely different do not behave ideally, and may be impossible to separate by ordinary distillation. The reason for this is that under certain conditions, the compositions of the liquid and of the vapor in equilibrium with it become identical, precluding any further separation. These cross-over points appear as "kinks" in the boiling point diagrams.

### High- and low-boiling azeotropes

Thus in this boiling point diagram for a mixture exhibiting a positive deviation from Raoult's law, successive fractionations of mixtures correspond to either ① or ② bring the distillation closer to the azeotropic composition indicated by the dashed vertical line. Once this point is reached, further distillation simply yields more of the same "high-boiling" azeotrope.



Distillation of a mixture having a negative deviation from Raoult's law leads to a similar stalemate, in this case yielding a "low-boiling" azeotrope. High- and low-boiling azeotropes are commonly referred to as *constant-boiling mixtures*, and they are more common than most people think.



### "Breaking" an azeotrope

There are four general ways of dealing with azeotropes. The first two of these are known collectively as *azeotropic distillation*.

- **Addition of a third substance** that alters the intermolecular attractions is the most common trick. The drawback is that another procedure is usually needed to remove this other substance.
- **Pressure-swing distillation** takes advantage of the fact that boiling point ( $T, X$ ) diagrams are two-dimensional slices of a ( $T, X, P$ ) diagram in which the pressure is the third variable. This means that the azeotropic composition depends on the pressure, so distillation at some pressure other than 1 atm may allow one to "jump" the azeotrope.
- **Use of a molecular sieve** — a porous material that selectively absorbs one of the liquids, most commonly water when the latter is present at a low concentration.
- **Give up.** It often happens that the azeotropic composition is sufficiently useful that it's not ordinarily worth the trouble of obtaining a more pure product. This accounts for the concentrations of many commercial chemicals such as mineral acids.

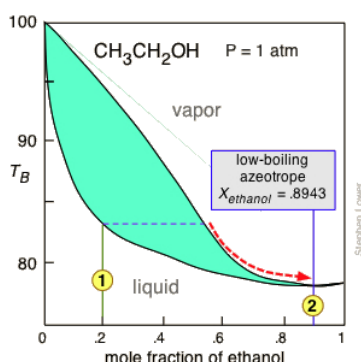
Some constant-boiling mixtures with water

mixture	azeotrope
Ethanol	98%, high, 78.1°C
Hydrochloric acid	20.2% high, 108.6°C
Hydrofluoric acid	35.6%, 111.3°C
Nitric acid	68%, 120.5°C



mixture	azeotrope
Sulfuric acid	98.3%, 338°C

Ethanol is one of the major industrial chemicals, and is of course the essential component of beverages that have been a part of civilization throughout recorded history. Most ethanol is produced by fermentation of the starch present in food grains, or of sugars formed by the enzymatic degradation of cellulose. Because ethanol is toxic to the organisms whose enzymes mediate the fermentation process, the ethanol concentration in the fermented mixture is usually limited to about 15%. The liquid phase of the mixture is then separated and distilled.



**Figure 8.9.8:**

*the normal boiling point of ethanol is 78.4°C, but its formation of a low-boiling azeotrope*

*with water limits the maximum concentration that can be obtained*

*b*

*y ordinary distillation to 95.6 volume-% (89.5 mole-%). This concentration is adequate for many applications, for which the product is commonly sold as "95% ethanol".*

*o  
l".*

For applications requiring anhydrous ethanol ("absolute ethanol"), the most common method is the use of zeolite-based molecular sieves to absorb the remaining water. Addition of benzene can break the azeotrope, and this was the most common production method in earlier years. For certain critical uses where the purest ethanol is required, it is synthesized directly from ethylene.

Here we briefly discuss two distillation methods that students are likely to encounter in more advanced organic lab courses.

**Vacuum distillation:** Many organic substances become unstable at high temperatures, tending to decompose, polymerize or react with other substances at temperatures around 200° C or higher. A liquid will boil when its vapor pressure becomes equal to the pressure of the gas above it, which is ordinarily that of the atmosphere. If this pressure is reduced, boiling can take place at a lower temperature. (Even pure water will boil at room temperature under a partial vacuum.) "Vacuum distillation" is of course a misnomer; a more accurate term would be "reduced-pressure distillation". Vacuum distillation is very commonly carried out in the laboratory and will be familiar to students who take more advanced organic lab courses. It is also sometimes employed on a large industrial scale.

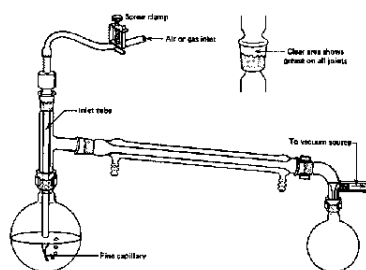


Fig. 100 A vacuum distillation setup.

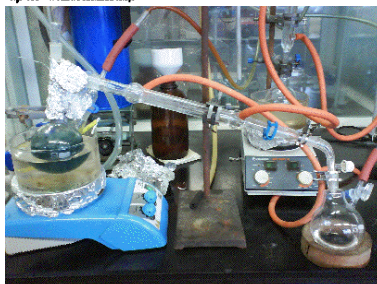


Figure 8.9.9: vacuum connection at lower right

The vacuum distillation setup is similar that employed in ordinary distillation, with a few additions:

- The vacuum line is connected to the bent adaptor above the receiving flask.
- In order to avoid uneven boiling and superheating ("bumping"), the boiling flask is usually provided with a fine capillary ("ebulliator") through which an air leak produces bubbles that nucleate the boiling liquid.
- The vacuum is usually supplied by a mechanical pump, or less commonly by a water aspirator or a "house vacuum" line.
- The boiling flask is preferably heated by a water- or steam bath, which provides more efficient heat transfer to the flask and avoids localized overheating. Prior to about 1960, open flames were commonly used in student laboratories, resulting in occasional fires that enlivened the afternoon, but detracted from the student's lab marks.
- A Claisen-type distillation head (below) provides a convenient means of accessing the boiling flask for inserting an air leak capillary or introducing additional liquid through a separatory funnel. This Claisen-Vigreux head includes a fractionation column.

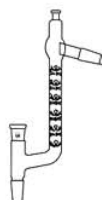


Figure 8.9.10: A Claisen-type distillation head

**Steam Distillation:** Strictly speaking, this topic does not belong in this unit, since steam distillation is used to separate *immiscible* liquids rather than solutions. But because immiscible liquid mixtures are not treated in elementary courses, we present a brief description of steam distillation here for the benefit of students who may encounter it in an organic lab course. A mixture of immiscible liquids will boil when their *combined* vapor pressures reach atmospheric pressure. This combined vapor pressure is just the sum of the vapor pressures of each liquid individually, and is independent of the quantities of each phase present.

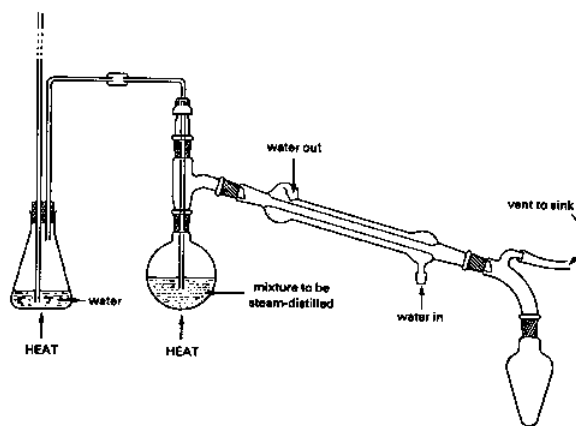


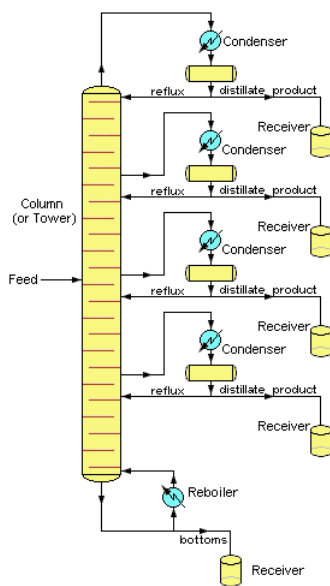
Figure 8.9.11

Because water boils at  $100^{\circ}\text{C}$ , a mixture of water and an immiscible liquid (an "oil"), even one that has a high boiling point, is guaranteed to boil *below*  $100^{\circ}\text{C}$ , so this method is especially valuable for separating high boiling liquids from mixtures containing non-volatile impurities. Of course the water-oil mixture in the receiving flask must itself be separated, but this is usually easily accomplished by means of a separatory funnel since their densities are ordinarily different.

There is a catch, however: the lower the vapor pressure of the oil, the greater is the quantity of water that co-distills with it. This is the reason for using steam: it provides a source of water able to continually restore that which is lost from the boiling flask. Steam distillation from a water-oil mixture without the introduction of additional steam will also work, and is actually used for some special purposes, but the yield of product will be very limited. Steam distillation is widely used in industries such as petroleum refining (where it is often called "steam stripping") and in the flavors-and-perfumes industry for the isolation of essential oils

The term *essential oil* refers to the aromas ("essences") of these [mostly simple] organic liquids which occur naturally in plants, from which they are isolated by steam distillation or solvent extraction. Steam distillation was invented in the 13th Century by Ibn al-Baitar, one of the greatest of the scientists and physicians of the Islamic Golden Age in Andalusia.

Distillation is one of the major "unit operations" of the chemical process industries, especially those connected with petroleum and biofuel refining, liquid air separation, and brewing. Laboratory distillations are typically batch operations and employ relatively simple fractionating columns to obtain a pure product. In contrast, industrial distillations are most often designed to produce mixtures having a desired boiling range rather than pure products.



Industrial operations commonly employ bubble-cap fractionating columns (seldom seen in laboratories), although packed columns are sometimes used. Perhaps the most distinctive feature of large scale industrial distillations is that they usually operate on a continuous basis in which the preheated crude mixture is preheated in a furnace and fed into the fractionating column at some intermediate point. A reboiler unit maintains the bottom temperature at a constant value. The higher-boiling components then move down to a level at which they vaporize, while the lighter (lower-boiling) material moves upward to condense at an appropriate point.

Petroleum is a complex mixture of many types of organic molecules, mostly hydrocarbons, that were formed by the effects of heat and pressure on plant materials (mostly algae) that grew in regions that the earth's tectonic movements buried over periods of millions of years. This mixture of liquid and gases migrates up through porous rock until it is trapped by an impermeable layer of sedimentary rock. The molecular composition of *crude oil* (the liquid fraction of petroleum) is highly variable, although its overall elemental makeup generally reflects that of typical plants.

element	carbon	hydrogen	nitrogen	oxygen	sulfur	metals
amount	83-87%	10-14%	0.1-2%	0.1-1.5%	0.5-6%	

The principal molecular constituents of crude oil are

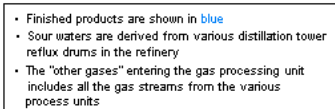
- alkanes: Also known as *paraffins*, these are saturated linear- or branched-chain molecules having the general formula  $C_nH_{2n+2}$  in which  $n$  is mostly between 5 and 40.
- unsaturated aliphatic: Linear- or branched chain molecules containing one or more double or triple bonds (alkenes or alkynes).
- Cycloalkanes: Also known as naphthenes these are saturated hydrocarbons  $C_nH_{2n}$  containing one or more ring structures.
- Aromatic hydrocarbons: These contain one or more fused benzene rings  $C_nH_n$ , often with hydrocarbon side-chains.

The word *gasoline* predates its use as a motor fuel; it was first used as a topical medicine to rid people of head lice, and to remove grease spots and stains from clothing. The first major step of refining is to fractionate the crude oil into various boiling ranges.

boiling range	fraction name	further processing
	butane and propane	gas processing
30 - 210°	straight-run gasoline	blending into motor gasoline
100 - 200°	naphtha	reforming into gasoline components
150 - 250°	kerosene	jet fuel blending
160 - 400°	light gas oil	distillate fuel blending into diesel or fuel oil
315 - 540°	heavy gas oil	catalytic cracking: large molecules are broken up into smaller ones and recycled
>450°	asphalts, bottoms	may be vacuum-distilled into more fractions

### Further processing and blending

About 16% of crude oil is diverted to the petrochemical industry where it is used to make ethylene and other feedstocks for plastics and similar products. Because the fraction of straight-run gasoline is inadequate to meet demand, some of the lighter fractions undergo reforming and the heavier ones cracking and are recycled into the gasoline stream. These processes necessitate a great amount of recycling and blending, into which must be built a considerable amount of flexibility in order to meet seasonal needs (more volatile gasolines and heating fuel oil in winter, more total gasoline volumes in the summer.)



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